PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D21H 13/26 | A1

(11) International Publication Number: WO 95/17549

(43) International Publication Date: 29 June 1995 (29.06.95)

(21) International Application Number: PCT/US94/14672

(22) International Filing Date: 20 December 1994 (20.12.94)

(30) Priority Data:
08/170,841 21 December 1993 (21.12.93) US

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: BURKS, Philip, Parks, Jr.; 8609 Old Brompton Road, Chesterfield, VA 23832 (US). HESLER, Lee, James; 8217 Surreywood Drive, Richmond, VA 23235 (US).

(74) Agents: TULLOCH, Rebecca, W. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States: BY, JP, KZ, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: LAYERED SMOOTH SURFACE ARAMID PAPERS OF HIGH STRENGTH AND PRINTABILITY

(57) Abstract

A multi-layered smooth surface aramid paper with high break strength and tear resistance comprises a substrate layer and at least one surface layer intimately bonded to the substrate layer, wherein the surface layer(s) consists essentially of 65 to 90 % by weight aramid fibrids and 10 to 35 % by weight aramid floc and comprises 10 to 67 % of the total basis weight of the paper.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

TITLE

LAYERED SMOOTH SURFACE ARAMID PAPERS OF HIGH STRENGTH AND PRINTABILITY

Background of the Invention

This invention relates to an improved layered aramid paper having a smooth surface and good tensile and tear strengths. The smooth surface provides for better print clarity and makes such papers particularly useful for high temperature label applications. Prior art techniques that improve on surface smoothness often lead to a reduced level of mechanical strength and/or thermal stability. Moreover, synthetic papers which have been pressed or calendered at high temperature and pressure will generally have fibers on the surface which cause roughness or snagging when the surface of the paper is worked during end use processing.

Summary of the Invention

This invention provides a multi-layered, smooth surface aramid paper containing from 40 to 55% by weight of fibrids and comprising a substrate layer which consists essentially of aramid fibrids and floc and one or two surface layers each intimately bonded to the substrate layer, said surface layer(s) consisting essentially of from 65 to 90% by weight aramid fibrids and from 10 to 35% by weight aramid floc and comprising from 10 to 67% of the weight of the paper. Preferably, the paper has a density of 0.8 to 1.0 g/cc with thickness of 1 to 30 mils (0.025 to 0.762 mm).

Detailed Description of the Invention

The multi-layered aramid papers of the invention are comprised of layers of different compositions to provide desired properties. The surface layer(s) provide a smooth surface and contain from 65 to 90% aramid fibrid and from 10% to 35% of aramid floc. The surface layer(s) constitutes from 10 to 67% of the weight of the paper. The substrate layer provides high tear strength. In order for

the multi-layered paper to behave as a unitary structure, it is preferred that the fibrous materials at the interface between layers be intermingled. This is achieved by depositing a layer of furnish, i.e., a paper-making aqueous dispersion of floc and fibrid on an undried, previously formed layer of furnish in a paper making machine or by simultaneously depositing the layers of different composition on the screen of the paper making machine using a 2 or 3 layer hydraulic type headbox. The paper coming off the machine is dried and calendered, preferably to a thickness of from 1 to 30 mils. The density of the layered paper is preferably from 0.8 to 1.0 g/cc for use as labels.

It has been found that the multi-layered papers of this invention have excellent mechanical properties. The smooth surface retains a high degree of smoothness even after the necessary working to prepare it for end use applications. This quality is important if print clarity and color density is to be achieved.

Aramid floc is high temperature resistant floc or short fiber cut from longer aramid fiber, such as those prepared by processes described in U.S. Pat. Nos. 3,063,966; 3,133,138; 3,767,756 and 3,869,430. It refers to short fibers typically having a length of 2 to 12 mm and a linear density of 1-10 decitex, made of aromatic polyamide which is non-fusible.

The aramid fibrids can be prepared using a fibridating apparatus where a polymer solution is precipitated and sheared in a single step as described in U.S. Pat. No. 3,756,908.

Tests and Measurements

Total Break Strength. The tensile break strength of paper is determined based on ASTM method D 828-87 for "Standard Test Method for Tensile Breaking Strength of Paper and Paperboard". Specimens are 2.54 cm wide and 20.3 cm long and the jaws of the tensile testing machine are initially separated by 12.7 cm. Ten paper samples are

tested in the machine direction (MD) and ten are tested in the cross direction (CD) and the values for each direction are averaged. The total of the MD and CD strengths is divided by paper density and paper basis weight to obtain the Total Break Strength.

Thickness. Thickness of papers is determined using calipers in accordance with ASTM D 374-79 (1986).

Density. Density of papers is determined by determining the weight per unit area of the paper (Basis Weight) in accordance with ASTM D 646-86 and dividing by the thickness.

Abraded Fiber Count.

In order to further investigate the abrasion qualities of these papers, the papers were folded and the edge of the fold was viewed against a dark background. The number of fibers extending greater than about 0.5 mm above the solid paper surface was taken as the Abraded Fiber Count (per centimeter) and indicates the degree of roughness of the sample.

The following examples are illustrative of the invention and are not to be construed as limiting.

EXAMPLES

Example 1

A two layered structure was made by combining fibrids of poly(m-phenylene isophthalamide) prepared as described in Example 1 of U.S. Pat. No. 3,756,908 and floc prepared by dry spinning poly(m-phenylene isophthalamide) from a solution containing 67% dimethyl acetamide (DMAc), 9% calcium chloride and 4% water. The spun filaments were flooded with an aqueous liquid and contained about 100% DMAc, 45% calcium chloride and 30-100% water based on dry polymer. The filaments were washed and drawn 4X in an extraction-draw process in which the chloride and DMAc contents were reduced to about 0.10% and 0.5%, respectively. The filaments had a denier of 2 (2.2 dtex) and typical properties were: elongation to break, 34%, and tenacity, 4.3 grams/denier (3.8 dN/tex). The filaments

were then cut to floc length of 0.27 inch (0.68 cm) and slurried in water to a concentration of about 0.35%.

Blends of fibrids and floc were separately fed to a 2-layer hydraulic type headbox which maintains each blend as a distinct layer until the slice exit where limited mixing of the layers occurs. This allows good bonding between the layers while still maintaining the individual nature of each layer. The formed sheet is then processed as is normally done on a fourdrinier paper machine by pressing and drying.

The papers are dried completely using infrared heaters before being calendered at 320°C at a line speed of 30 feet per minute (9 meters per minute) using a pressure of 725 pounds per linear inch (130 kg/cm).

The composition of the layers varied from 35 to 65% fibrid, the remainder being floc. The basis weight of each layer was adjusted so that the high fibrid layer (65% fibrid) ranged from 33 to 67% of the total basis weight of the final sheet. The total fibrid content of the test papers ranged from 45 to 55% of the sheet versus 53% for the single layer control papers (C1-1). Table 1 gives the basis weight of each layer and its composition.

Table 1

	Total Sheet			Substrate Layer			Surface Layer		
Run Number	BW aim g/m^2	% Fibrid	% Floc	BW aim g/m^2	% Fibrid	% Floc	BW aim g/m^2	% Fibrid	% Floc
1-1	42	45	55	28	35	65	14	65	35
1-2	42	50	50	21	35	65	21	65	35
1-3	42	55	45	14	35	65	28	65	35
C1-1	42	53	47	42	53	47	-	-	-

The amount of loose fibers on the surfaces of the sheet as a result of mechanical working of the calendered paper was measured (Table 2). Side 1 is the substrate layer (low fibrid content layer) and Side 2 the surface (high fibrid content) layer.

Table 2

Abraded Fiber Count

Sample Number	Fiber Count (per 5 cm) Side 1	Side 2
1-1	20	0
1-2	12	2
1-3	14	0
C1-1	14	-

Even with the significant reduction in the number of loose fibers on the surface of the high fibrid content papers, superior mechanical properties are maintained versus a control paper of similar average composition but with no layering (Table 3).

Table 3

Calendered Paper Properties

Sample Number	1-1	1-2	1-3	C1-1
B.W.*, oz/yd^2	1.3	1.5	1.4	1.3
(g/m^2)	(44.1)	(50.9)	(47.5)	(44.1)
Thickness, mils	2.0	2.5	2.2	2.4
(mm)	(0.051)	(0.064)	(0.056)	(0.061)
Density, g/cc	0.82	0.89	0.86	0.72
B.S.**, lb/in MD/CD	15/7	21/10	18/7	20/8
(N/cm)	(26/12)	(37/18)	(32/12)	(35/14)
Eb***, MD/CD	4/3	6/3	5/2	6/3
Elmendorf Tear, g MD/CD	108/191	120/193	87/166	127/215
(N)	(1.06/1.87)	(1.18/1.89)	(0.85/1.63)	(1.25/2.11)
Shrinkage @ 300°C, % MD/CD	2/0	2/0	2/0	2/0

* Basis Weight

** Break Strength

*** Break Elongation

Example 2

Layered structures, 4.0-4.5 oz/yd^2 (135.6-152.6 g/m^2) were produced with high fibrid layers on both top and bottom of the structure. The top and bottom plies (outer layers) had equal basis weight. The top and bottom layers contain 65% fibrid and 35% floc. The top layer was applied using a secondary headbox jetting the furnish onto an already formed sheet which was prepared using the headbox of Example 1. The control (C2-1) was a single layer paper.

Table 4

	Total Sheet			Each Outer Layer			Inner (Substrate) Layer		
Run Number	BW aim g/m^2	% Fibrid	% Floc	BW aim g/m^2	% Fibrid	% Floc	BW aim g/m^2	% Fibrid	% Floc
2-1	132	46	54	24	65	35	84	35	65
2-2	132	55	45	44	65	35	44	35	65
C2-1	137	47	137	53	47	-	-	-	-

Improvement in the amount of loose fibers on the surface as a result of mechanical working of the paper is obvious from Table 5.

Table 5
Abraded Fiber Count

Sample Number	Fiber Count (per 5 cm)
2-1	5
2-2	7
C2-1	12

Even with the major reduction in the number of loose fibers on the surface of the papers superior mechanical properties are maintained versus a control paper of similar average composition but with no layering

(Table 6). The low shrinkage at 300°C along with the high tear and tensile properties as compared with the control is especially noteworthy.

Table 6

Calendered Paper Properties

Sample Number	2-1	2-2	C2-1
Basis Weight, oz/yd^2	4.3	4.3	4.1
(g/m^2)	(145.7)	(145.8)	(139.0)
Thickness, mils	7.5	6.7	6.8
(mm)	(0.191)	(0.170)	(0.173)
Density, g/cc	0.77	0.87	0.80
B.S., lb/in MD/CD	55/30	61/39	54/33
(N/cm)	(96/53)	(107/68)	(95/58)
Eb, % MD/CD	6/4	9/6	7/5
Elmendorf Tear, g MD/CD	695/762	421/598	504/662
(N)	(6.82/7.48)	(4.13/5.87)	(4.94/6.49)
Shrinkage @300°C, % MD/CD	1/1	1/1	1/1

Claims:

1. A multi-layered smooth surface aramid paper containing from 40 to 55% by weight of fibrids and comprising a substrate layer which consists essentially of aramid fibrids and floc and one or two surface layers, each intimately bonded to the substrate layer, said surface layer(s) comprising from 10 to 67% of the weight of the paper and consisting essentially of from 65 to 90% by weight aramid fibrids and from 10 to 35% by weight aramid floc;

2. The paper of Claim 1 having a density of 0.8 to 1.0 g/cc and a thickness of 1 to 30 mils (0.0254 to 0.762 mm).

3. The paper of Claim 1, wherein said paper comprises two surface layers intimately bonded to opposite sides of said substrate layer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/14672

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H13/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,94 16142 (DU PONT DE NEMOURS) 21 July 1994 *The entire abstract*	1-3
X	US,A,5 089 088 (G.L.HENDREN ET AL) 18 February 1992 see claims 1-6	1-3
A	US,A,5 076 887 (G.L.HENDREN) 31 December 1991 see claims 1-17	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 April 1995	18.04.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Fouquier, J-P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/14672

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9416142	21-07-94	NONE	
US-A-5089088	18-02-92	JP-A- 6047759	22-02-94
US-A-5076887	31-12-91	JP-A- 4257400	11-09-92